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Jun 22, 1993

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TITLE: Ornamental component mfr. for watch exteriors with good wear resistance - by applying coating to surface of stock, laser machining to form concave letters and patterns, applying different coloured layer, etc.

PATENT-ASSIGNEE: SEIKO EPSON CORP (SHIH)

PRIORITY-DATA: 1991JP-0319268 (December 3, 1991)

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ABSTRACTED-PUB-NO: JP 05156425A

BASIC-ABSTRACT:

Component is made by applying a colour coating, as the 1st layer, on the surface of a stock by dry film forming process, laser machining selective given parts to form concave letters and/or patterns with a depth over the thickness of the 1st layer, having components different from those on the 1st layer by dry film forming process, followed by finishing the surface by removing the two layers except the letters and/or patterns by etching.

USE - Used for exterior components for watches, having stable quality, excellent corrosion resistance, coating adherence and wear resistance.

ABSTRACTED-PUB-NO: JP 05156425A

EQUIVALENT-ABSTRACTS:

CHOSEN-DRAWING: Dwg.0/4

DERWENT-CLASS: M13 P55 P78

CPI-CODES: M13-H; M14-A; M23-D05;

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(71)Applicant : SEIKO EPSON CORP

(22)Date of filing : 03.12.1991

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(54) ORNAMENTAL MEMBER AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To improve the appearance and quality and to reduce cost by forming a recessed letter, etc., coated with a colored film on the surface of a base material of Pt alloy, etc., by a dry film forming method.

CONSTITUTION: A recessed letter and/or pattern coated with a colored film is formed on the surface of a base material such as sintered hard alloy, Pt, Pt alloy, ceramic and white gold alloy by a dry film forming method. The material surface is coated with a colored film as a first layer, a recessed pattern having a depth greater than the thickness of the first layer is formed on the specified part by laser beam machining, then the colored film having a different composition from that of the first layer is applied as a second layer by a dry film forming method, and then the first and second layers other than the patterned part is etched off. Consequently, an ornamental member having a stable quality is provided at a low cost.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the ornament member and the manufacture approach that multiple color was made to the appearance of the exterior parts for clocks, glasses components, a writer case, etc.

[0002]

[Summary of the Invention] This invention is in the place which offers stably in quality an ornament member with the high decorative value excellent in the corrosion resistance which has the concave alphabetic character and/or concave pattern which covered the colored coat with the dry type forming-membranes method on the material of superhard, Pt, Pt alloy, a ceramic, and a white gold alloy, adhesion, and abrasion resistance cheaply.

[0003]

[Description of the Prior Art] The concave pattern in ornament members, such as the conventional exterior parts for clocks, and/or the appearance color tone of the alphabetic character section and the other front face as the manufacture approach of the product changed and multiple-color-ized Wet plating of gold plate etc. is performed to the whole material front face, such as SUS which has a pattern that it was beforehand formed in the concave, and/or an alphabetic character. **** -- How to carry out exfoliation removal of the wet plating of those other than the masking section, and to remove a masking coating further after printing a pattern or the alphabetic character section using the masking coating for plating.

[0004] ** How to multiple-color-ize a surface of metal by printing into the concave pattern beforehand formed on the metal material of pad printing or screen-stencil like the open patent official report 64-75660, and parts other than an alphabetic character, forming a coat in after an appropriate time by the ion plating method, and removing a printing coat.

[0005] ** How to carry out dissolution removal of the deposit, after applying an organic resist to dry type plating garbages other than a concave, carrying out dissolution removal of the deposit after baking hardening, after forming the deposit of nickel plating, coppering, or its alloy all over a substrate like the open patent official report Showa 61-117269, carrying out dissolution removal of the organic resist after that and making a dry type deposit form subsequently. ** -- it is general.

[0006]

[Problem(s) to be Solved by the Invention] However, there are the following faults in the above-mentioned conventional technique.

** By the approach, wet plating processing of a pattern that it is the design point, and the alphabetic character section is carried out, and since the coat degree of hardness is as low as Hv 200-300, the pattern that the area in a crevice is large, and an alphabetic character tend to receive wear or a crack, and have a big fault as accessories that a pattern that it is based on soft wet plating finishing of a crevice, and an alphabetic character appearance fall remarkably by the crack and wear.

[0007] ** By the approach, since the temperature on the front face of a substrate rises under the effect of

the radiant heat by the dissolution of an evaporation metal during ion plating processing, the gas which is inherent in masking, and the cracked gas of masking occur as emission gas during ion plating processing, it has a bad influence on generation of an ion plating coat, and the interference color of a coat, color nonuniformity or discharge, and poor adhesion occur. Moreover, it was easy to spoil the purpose appearance that it is easy to produce the chip of the masking periphery section, and exfoliation. For this reason, mass-production nature had the remarkably low bad rate of an excellent article, and there was a fault which becomes a cost rise.

[0008] ** By the approach, over-etching to the bottom of the resist film occurs in deposit exfoliation of the nickel-plating layer after resist spreading etc. Moreover, nickel, copper, or its alloy carries out thermal diffusion to a substrate front face with the heat generated at the time of dry type plating, and discoloration on the front face of a substrate occurs. Moreover, deposit exfoliation removal of the nickel-plating layer after dry type plating etc. took long duration, and there was a fault with bad working efficiency.

[0009] Furthermore, in the approach of ** - **, although it was common to have used etching as for a concave pattern or a concave alphabetic character, it had the fault limited to materials, such as a zinc alloy, a copper alloy, and an iron alloy. Furthermore, since the masking process at the time of etching and the masking process at the time of two-color-izing of a crevice and the other part were required, there were many defect factors, such as location gap, and they had the fault with it. [the remarkable rate of an excellent article, and] [low]

[0010] The place which this invention solves such ***** and is made into the purpose The improvement in the rate of an excellent article and the cost cut by masking process abolition, superhard, Pt, In the former, such as Pt alloy, a ceramic, and a white gold alloy, the concave pattern by etching or a concave pattern complicated also about the material for which formation of an alphabetic character was difficult, and/or an alphabetic character are formed. It is in the place which offers an ornament member with the high decorative value excellent in the adhesion which furthermore made the crevice colored, corrosion resistance, abrasion-proof nature, and abrasion resistance, and its manufacture approach.

[0011]

[Means for Solving the Problem] The ornament member of this invention is characterized by having the concave alphabetic character and/or concave pattern which covered the colored coat with the dry type forming-membranes method on the material front face of superhard, Pt, Pt alloy, a ceramic, and a white gold alloy. After covering a colored coat with the dry type forming-membranes method as the first pass on this material front face, into an alternative predetermined part by laser processing A concave alphabetic character and/or a concave pattern are formed in the depth exceeding the coat thickness of the first pass, and it is characterized by carrying out the covering laminating of the colored coat of a different component from the first pass, then carrying out exfoliation removal of the first passes other than an alphabetic character and/or the encaustic section, and the second layer by etching, and finishing as the second layer after that.

[0012]

[Function] The hard coat by the dry type forming-membranes method for having excelled in abrasion-proof nature and abrasion resistance as the last finishing at the design point section as accessories of a pattern that the front face is formed in the concave, or the alphabetic character section is made to form, and the fall of an appearance is not caused for a pattern that it is an ornamental appeal point, and an alphabetic character, by long-term cellular phone, either, but it enables it to maintain the ornament appearance of the time of a product according to the above-mentioned configuration of this invention. Furthermore, while enabling adhesion reservation of the colored coat to a material top, such as superhard and a ceramic, concave color tone variety can be measured easily.

[0013] Next, the manufacture approach of this invention ornament member is described. By having covered the colored coat with the dry type forming-membranes method as the first pass on the material, since this whole member front face is masked with a hard coat, this bill-of-materials side becomes possible [preventing the adhesion and the blemish of YAKE in the laser-processing process of degree process]. In the colored coat covering process of a different component from the first pass after laser

processing, since the base of superhard, Pt, Pt alloy, a ceramic, and a white gold alloy is exposed, the good coat configuration of adhesion is possible for the concave pattern or the concave alphabetic character section by laser processing like the dry type forming-membranes method to this material top currently generally performed. By having carried out the laminating of the coat with which the components by the dry type forming-membranes method differ to the first pass and the second layer, generally, since the coat by the dry type forming-membranes method has many pinholes, in a back process, the exfoliation liquid for the first passes permeates through the pinhole of the second layer coat, a first pass coat exfoliates, and the lift rise of the second layer coat of parts other than a crevice can be carried out at coincidence, and it can exfoliate easily. Since the second layer coat in a crevice differs in the first pass coat and the component at this time, there is no degradation of adhesion with the exfoliation liquid for the first passes and an appearance. Next, as a colored coat by the dry type forming-membranes method, noble metals and alloys with at least one or more components with C, N, and O which use Ti, Zr, Hf, V, Nb, Ta, Cr, W, etc. as a principal component, such as a compound, or Au, Pt, Pd, Ag, can be applied. As a dry type forming-membranes method, PVD or CVD methods, such as vacuum evaporation technique, the sputtering method, and the ion plating method, can be applied. Hereafter, this invention is explained based on an example.

[0014]

[Example]

(Example 1) Drawing 1 (a) - (d) is a sectional view in each production process of the clock housing created by this invention. First, the clock housing 1 formed with the superhard ingredient of WC shown in drawing 1 R> 1 (a) was attached in the vacuum chamber of an ion plating system, the inside of a vacuum chamber was eliminated, ion bombardment was performed for Ar gas with the applied voltage of 0.5kV to 10Pa and a substrate in advance of the process which subsequently carries out ion plating processing of this clock housing, and the clock housing front face was cleaned. Next, after discharging Ar gas and returning the inside of a vacuum chamber to 3×10^{-2} Pa, introduced N₂ gas up to 6×10^{-2} Pa as reactant gas anew, impress 0.1kV of substrate electrical potential differences, generated the plasma, coincidence was made to carry out heating evaporation of the metal Cr with an electron-beam-heating method, and 1.0 micrometers of CrN coats 2 of the stainless steel color which is the compound of Cr and N were covered. Next, marking of the concave alphabetic character was carried out to the depth which exceeds CrN coat thickness in a predetermined part by laser processing as shown in drawing 1 (b). For this reason, WC superhard material has exposed the front face of the laser-processing alphabetic character 3. In this laser processing, it was processed on output 100W and the conditions of 10ms of pulse width using commercial Nd= YAG laser equipment (wavelength of 1.06 micrometers). Next, as shown in drawing 1 R> 1 (c), 1.0 micrometers of golden TiNC layers 4 which made Ti the evaporation source by the same ion plating method as the above-mentioned all over the clock housing of the condition of drawing 1 (b), and made reactant gas N₂ gas and C₂H₂ gas were covered.

[0015] Next, the clock housing of the condition which shows in drawing 1 (c) was immersed into the sodium-carbonate water solution, clock housing was made into the anode plate, the direct current of 5V was energized and etching removal of the CrN layer 2 was carried out. At this time, the lift rise also of TiNC4 on the CrN layer 2 was carried out, it was removed by coincidence, and the clock housing made from WC superhard with which the concave alphabetic character which presents the golden appearance by the TiNC compound coat 4 to the predetermined part of the clock housing 1 made from WC superhard as finally shown in drawing 1 (d) is given, and others present the two-color appearance of a superhard material color was acquired. WC superhard clock housing manufactured by this approach An artificial sweat corrosion test (40 degreeCx humidity 90% \times 48Hr), artificial sea water (40 degreeCx humidity 90% \times 48Hr), a bending test (180-degree bending) and a heat shock trial (300 degreeCx 10 minute heating -> water quenching --) A 5 times repeat, an antifriction trial (500g load is applied to clock housing on cowhide) The abrasion-proof trial (it falls [on vinytile] repeatedly 20 times from 1m) which rubs the two-color boundary section of clock housing 30,000 times by 5cm stroke was performed, and all the above-mentioned test results were what satisfies enough the corrosion resistance as clock housing, adhesion, abrasion resistance, and abrasion-proof nature.

[0016] (Example 2) Drawing 2 (a) - (d) is the sectional view of the clock housing for every production process of this invention example.

[0017] First, 0.5 micrometers of metal Ti layers 6 were covered with the ion plating method on the whole front face of the clock housing 5 which consists of a Pt (Pt95wt%-Cu) alloy as shown in drawing 2 (a). Next, as shown in drawing 2 (b), the concave pattern 7 was formed in the predetermined part of clock housing by laser processing of an example 1 and these conditions. Next, as shown in drawing 2 (c), 1.5 micrometers of CrNCO layers 8 of the ashes black by the ion plating method were covered on the whole surface. next, the clock housing of the condition of drawing 2 (c) -- fluoric acid: -- into the mixed liquor (ordinary temperature) of nitric-acid =1:1, it ****(ed) for about 1 minute and etching removal of the Ti layer 6 was carried out. At this time, the lift rise was carried out at coincidence and the CrNCO layer 8 on the Ti layer 6 was also removed finely. The clock housing which presents the two-color appearance by the concave pattern which presents the ashes black by CrNCO to the predetermined part of Pt alloy clock housing front face as this finally shows to drawing 2 (d), and the white of Pt alloy was formed. This clock housing has satisfied enough the corrosion resistance as clock housing, abrasion resistance, and abrasion-proof nature as a result of the same qualification test as [an example 1].

[0018] (Example 3) Drawing 3 is the sectional view of the clock housing of this invention example. 1.0 micrometers of CrN coats were covered on the whole front face of the clock housing 9 which consists of a white gold alloy (Au75%-Ag-Pd) like [the example 1], and the same concave alphabetic character 3 as the predetermined part of clock housing was formed in it by laser processing. Next, 1.5 micrometers of TiO layers 10 of the blue system by the ion plating method were covered. Next, etching removal of the CrN layer was carried out by the example 1 and this approach. At this time, the lift rise was carried out at coincidence and the TiO layer on a CrN layer was also removed finely. The clock housing which has a two-color appearance by the concave alphabetic character and concave white gold alloy material which present the blue system by TiO to the predetermined part of a white gold alloy clock housing front face as this finally shows drawing 3 was formed. This clock housing has satisfied enough the corrosion resistance as clock housing, abrasion resistance, and abrasion-proof nature as a result of the same qualification test as an example 1.

[0019] (Example 4) Drawing 4 is the sectional view of the clock housing of this invention example. 1.0 micrometers of Ti coats were covered on the whole front face of the clock housing 11 which consists of ZrO₂ ceramic like the example 2, and the same concave pattern 7 as the predetermined part of clock housing was formed in it by laser processing. Next, 1.5 micrometers of CrNC coats 12 by the ion plating method were covered. Next, etching removal of the Ti layer was carried out by the example 2 and this approach. At this time, the lift rise was carried out at coincidence and the CrNC layer on Ti layer was also removed finely. As this finally showed drawing 4, the clock housing which has a two-color appearance by the concave pattern and concave ceramic material which present the stainless steel color by CrNC to the predetermined part of a ceramic clock housing front face was formed. This clock housing has satisfied enough the corrosion resistance as clock housing, abrasion resistance, and abrasion-proof nature as a result of the same qualification test as an example 1.

[0020]

[Effect of the Invention] As stated above, according to this invention, superhard, Pt, Pt alloy, a ceramic, After covering a kind of Ti system or the Cr system coats with the ion plating method as the first pass on a white gold alloy material An alphabetic character [moreover] is formed. an alternative predetermined part -- laser processing -- a concave pattern -- A first pass coat covers Cr system coat with Ti system as the second layer by the ion plating method after that. When a first pass coat covers the colored coat of Ti system with Cr system and carries out exfoliation removal of the first pass coat of Ti system or Cr system by etching succeeding Degradation and the cost rise of appearance quality which were the fault of a conventional method are improved. It became possible to offer stably cheaply in quality the ornament member with high decorative value which presents the two-color appearance which formed in the front face of an ornament member the concave pattern or concave alphabetic character which has colored [of requests, such as a complicated configuration,], and made the material color to other parts. Of course in application, exterior parts for clocks, such as a dial for clocks, a needle, and a band, are

applicable to all ornament components, such as a glasses frame, a writer, a tiepin, and accessories.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The sectional view showing each production process of the example of the exterior parts for clocks by this invention.

[Drawing 2] The sectional view showing each production process of the example of the exterior parts for clocks by this invention.

[Drawing 3] The sectional view of the exterior parts for clocks by this invention example.

[Drawing 4] The sectional view of the exterior parts for clocks by this invention example.

[Description of Notations]

1 Carbide (WC)

2 CrN Coat

3 Laser-Processing Alphanumeric Character

4 Golden TiNC Coat

5 Pt Alloy (Pt-Cu)

6 Ti Coat

7 Laser-Processing Pattern

8 Ashes Black CrNCO Coat

9 White Gold Alloy (Au-Ag-Pd)

10 Blue System TiO Coat

11 Ceramic (ZrO₂)

12 Stainless Steel Color CrNC Coat

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CLAIMS

[Claim(s)]

[Claim 1] The ornament member characterized by having the concave alphabetic character and/or concave pattern which covered the colored coat with the dry type forming-membranes method on the material front face of superhard, Pt, Pt alloy, a ceramic, and a white gold alloy.

[Claim 2] After covering a colored coat with the dry type forming-membranes method as the first pass on this material front face, into an alternative predetermined part by laser processing A concave alphabetic character and/or a concave pattern are constituted in the depth exceeding the coat thickness of the first pass. After that as the second layer The manufacture approach of the ornament member according to claim 1 characterized by carrying out the covering configuration of the colored coat of the component which differs from the first pass by the dry type forming-membranes method, then carrying out exfoliation removal of the first passes other than an alphabetic character and/or the encaustic section, and the second layer by etching, and finishing.

[Translation done.]

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(54)【発明の名称】 装飾部材およびその製造方法

(57)【要約】

【目的】 本発明は、湿式エッチング困難な合金素材上に乾式成膜法により有色被膜を被覆した凹状の文字および／または模様を有する装飾部材を提供する。

【構成】 超硬、Pt、Pt合金、セラミック、白色金合金素材上の選択的所定部分にレーザー加工により形成された凹状の文字および／または模様部に被覆された乾式成膜法による有色被膜と凹以外の素材色との二色に構成されていることを特徴とする。

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【特許請求の範囲】

【請求項1】超硬、Pt、Pt合金、セラミック、白色金合金の素材表面上に乾式成膜法により有色被膜を被覆した凹状の文字および／または模様を有する事を特徴とする装飾部材。

【請求項2】該素材表面上に第一層として乾式成膜法により有色被膜を被覆した後に、選択的所定部分にレーザー加工により、第一層の被膜厚みを越える深さに凹状の文字および／または模様を構成し、その後第二層として、乾式成膜法により第一層と異なる成分の有色被膜を被覆構成し、次にエッチングにより文字および／または模様部以外の第一層および第二層を剥離除去して仕上げる事を特徴とする請求項1記載の装飾部材の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、時計用外装部品、メガネ部品、ライターケース等の外観が多色に仕上げられた装飾部材および製造方法に関する。

【0002】

【発明の概要】本発明は、超硬、Pt、Pt合金、セラミック、白色金合金の素材上に乾式成膜法により有色被膜を被覆した凹状の文字および／または模様を有する耐食性、密着性、耐摩耗性に優れた装飾的価値の高い装飾部材を品質的に安定で、且つ安価に提供するところにある。

【0003】

【従来の技術】従来の時計用外装部品等の装飾部材における凹状の模様および／または文字部とそれ以外の表面との外観色調を変え多色化された製品の製造方法としては

① あらかじめ凹状に形成された模様および／または文字を有するSUS等の素材表面の全体に金メッキ等の湿式メッキを施し、メッキ用マスキング塗料を用い模様または文字部を印刷した後、マスキング部以外の湿式メッキを剥離除去し、さらにマスキング塗料を除去する方法。

【0004】② 公開特許公報64-75660の如く、パッド印刷またはスクリーン印刷により金属素材上にあらかじめ形成された凹状の模様、文字以外の部分に印刷し、しかる後にイオンブレーティング法により被膜を形成し、印刷被膜を剥すことにより金属表面を多色化する方法。

【0005】③ 公開特許公報昭61-117269の如く、基板全面にニッケルメッキまたは銅メッキまたはその合金のメッキ層を形成した後、凹状以外の乾式メッキ不要部分に有機質レジストを塗布し焼成硬化後メッキ層を溶解除去し、その後有機質レジストを溶解除去し、ついで乾式メッキ層を形成させた後、メッキ層を溶解除去する方法。が一般的である。

【0006】

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【発明が解決しようとする課題】しかし、前述の従来技術においては、以下の欠点がある。

①の方法ではデザインポイントである模様、文字部が湿式メッキ処理され被膜硬度がHv200～300と低いいため、凹部内の面積が大きい模様、文字は摩耗またはキズを受けやすく、凹部の軟らかい湿式メッキ仕上げによる模様および文字外観がキズおよび摩耗により著しく低下するという装飾品としての大きな欠点がある。

【0007】②の方法では、イオンブレーティング処理中に蒸発金属の溶解による輻射熱の影響で基板表面の温度が上昇するためマスキングに内在するガスやマスキングの分解ガスがイオンブレーティング処理中に放出ガスとして発生し、イオンブレーティング被膜の生成に悪影響を与え被膜の干渉色や色ムラ、あるいは放電、密着不良が発生する。またマスキング外周部の欠けや剥離が生じやすく目的外観を損ない易かった。この為良品率が著しく低く量産性が悪く、コストアップになる欠点があった。

【0008】③の方法では、レジスト塗布後のニッケルメッキ層等のメッキ層剥離にレジスト膜下へのオーバーエッチが発生する。また、乾式メッキ時に発生する熱によりニッケル、銅またはその合金が基板表面に熱拡散し、基板表面の変色が発生する。また、乾式メッキ後のニッケルメッキ層などのメッキ層剥離除去に長時間を要し作業効率が悪い欠点があった。

【0009】さらに、①～③の方法において、凹状の模様または文字は、エッチングを利用するのが一般的であるが、亜鉛合金、銅合金、鉄合金等の素材に限定されてしまう欠点を有していた。さらに、エッチング時のマスキング工程および凹部とそれ以外の部分の二色化時のマスキング工程が必要であるため、位置ズレ等の不良要因が多く、良品率が著しく低い欠点を有していた。

【0010】本発明は、このような問題点をを解決するもので、その目的とするところは、マスキング工程廃止による良品率向上およびコストダウンと超硬、Pt、Pt合金、セラミック、白色金合金等従来ではエッチングによる凹状の模様または文字の形成が困難であった素材についても複雑な凹状の模様および／または文字を形成し、さらに凹部を有色化した密着性、耐食性、耐擦傷性および耐摩耗性に優れた装飾的価値の高い装飾部材およびその製造方法を提供するところにある。

【0011】

【課題を解決するための手段】本発明の装飾部材は、超硬、Pt、Pt合金、セラミック、白色金合金の素材表面上に乾式成膜法により有色の被膜を被覆した凹状の文字および／または模様を有することを特徴とし、該素材表面上に第一層として乾式成膜法により有色被膜を被覆した後に、選択的所定部分にレーザー加工により、第一層の被膜厚みを越える深さに凹状の文字および／または模様を形成し、その後第二層として、第一層と異なる成

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分の有色被膜を被覆積層し、次にエッチングにより文字および/または模様部以外の第一層および第二層を剥離除去して仕上げることを特徴とする。

【0012】

【作用】本発明の上記構成によれば、表面が凹状に形成されている模様または文字部の装飾品としてのデザインポイント部に最終仕上げとして耐擦傷性および耐摩耗性に優れた乾式成膜法による硬質被膜を形成させており、装飾のアピールポイントである模様、文字を長期の携帯によっても外観の低下をおこさず製品当初の装飾外観を維持出来るようにしている。さらに、超硬、セラミック等の素材上への有色被膜の密着性確保を可能にするとともに凹状の色調バラエティーが容易にはかれる。

【0013】次に本発明装飾部材の製造方法について述べる。素材上に第一層として乾式成膜法により有色の被膜を被覆したことにより、該部材表面全体が硬質被膜でマスキングされるため該部材表面は次工程のレーザー加工工程におけるヤケの付着や傷を防止することが可能となる。レーザー加工後の第一層と異なる成分の有色被膜被覆工程においては、レーザー加工による凹状の模様または文字部は、超硬、Pt、Pt合金、セラミック、白色合金の素地が露出しているため一般的に行われている該素材上への乾式成膜法と同様に密着性の良い被膜構成が可能である。第一層および第二層に乾式成膜法による成分の異なる被膜を積層したことにより、一般に乾式成膜法による被膜はピンホールが多いことから後工程において第二層被膜のピンホールを介して第一層用の剥離液が浸透し、第一層被膜が剥離され同時に凹部以外の部分の第二層被膜はリフトアップし容易に剥離することができる。このとき凹部内の第二層被膜は第一層被膜と成分を異にしているため、第一層用の剥離液による密着性および外観の劣化は全くない。次に乾式成膜法による有色被膜としては、Ti、Zr、Hf、V、Nb、Ta、Cr、W等を主成分とするC、N、Oとの少なくとも一成分以上との化合物またはAu、Pt、Pd、Ag等の貴金属および合金が適用できうる。乾式成膜法としては真空蒸着法、スパッタリング法、イオンプレーティング法等のPVD法またはCVD法が適用できうる。以下、本発明について実施例に基づいて説明する。

【0014】

【実施例】

(実施例1) 図1(a)～(d)は本発明により作成した時計ケースの各製造工程での断面図である。まず、図1(a)に示すWCの超硬材料により形成された時計ケース1をイオンプレーティング装置の真空室内に取り付け、真空室内を排し、ついで該時計ケースをイオンプレーティング処理する工程に先立ちArガスを10Pa、基板への印加電圧0.5KVでイオンボンバードメントを行い時計ケース表面のクリーニングを行った。次にArガスを排出し真空室内を 3×10^{-2} Paに戻した後、

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改めて反応性ガスとしてN₂ガスを 6×10^{-2} Paまで導入し、基板電圧を0.1KV印加しプラズマを発生させ、同時に金属Crを電子ビーム加熱方式により加熱蒸発させ、CrとNとの化合物であるステンレス色のCrN被膜2を1.0μm被覆した。次に図1(b)に示すようにレーザー加工により所定部分において、CrN被膜厚を越える深さに凹状の文字をマーキングした。この為レーザー加工文字3の表面はWC超硬素材が露出している。該レーザー加工においては市販のNd=YAGレーザー装置(波長1.06μm)を用い、出力100W、パルス幅10msの条件にて加工を行った。次に図1(c)に示すように、図1(b)の状態の時計ケース全面に前述と同様のイオンプレーティング法によりTiを蒸発源としN₂ガスとC₂H₂ガスを反応ガスとした金色のTiNC層4を1.0μm被覆した。

【0015】次に図1(c)に示す状態の時計ケースを炭酸ナトリウム水溶液中に浸漬し、時計ケースを陽極にし5Vの直流電流を通電しCrN層2をエッチング除去した。このときCrN層2の上のTiNC4もリフトアップされ同時に除去され、最終的に図1(d)に示すようにWC超硬製時計ケース1の所定部分にTiNC化合物被膜4による金色外観を呈する凹状の文字が施され他が超硬素材色の二色外観を呈するWC超硬製時計ケースが得られた。この方法にて製作したWC超硬時計ケースは、人工汗耐食試験(40°C×湿度90%×48Hr)、人工海水(40°C×湿度90%×48Hr)、折り曲げ試験(180°折り曲げ)、熱ショック試験(300°C×10分加熱→水中急冷、5回繰り返し)、耐摩耗試験(牛革上にて500g荷重を時計ケースにかけ、5cmストロークにて時計ケースの二色境界部を3万回擦りつける)、耐擦傷試験(ビニタイル上1mより20回繰り返し落下する)を行い上記試験結果はすべて時計ケースとしての耐食性、密着性、耐摩耗性、耐擦傷性を充分満足するものであった。

【0016】(実施例2) 図2(a)～(d)は本発明実施例の各製造工程毎の時計ケースの断面図である。

【0017】まず、図2(a)に示すようにPt(Pt95wt%-Cu)合金よりなる時計ケース5の表面全体に金属Ti層6をイオンプレーティング法により0.5μm被覆した。次に図2(b)に示すように実施例1と同条件のレーザー加工により時計ケースの所定部分に凹状の模様7を形成した。次に図2(c)に示すように全面にイオンプレーティング法による灰黒色のCrNC層8を1.5μm被覆した。次に図2(c)の状態の時計ケースを硝酸:硝酸=1:1の混合液(常温)中に約1分浸漬しTi層6をエッチング除去した。このときTi層6上のCrNC層8も同時にリフトアップされきれいに除去された。これにより最終的に図2(d)に示すようなPt合金時計ケース表面の所定部分にCrNCによる灰黒色を呈する凹状の模様とPt合金の白色

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による二色外観を呈する時計ケースが形成された。該時計ケースは【実施例1】と同様の品質試験の結果、時計ケースとしての耐食性、耐摩耗性、耐擦傷性を十分満足できた。

【0018】(実施例3) 図3は本発明実施例の時計ケースの断面図である。白色金合金(Au75%-Ag-Pd)よりなる時計ケース9の表面全体に、【実施例1】と同様にCrN被膜を1.0 μ m被覆し、レーザー加工により時計ケースの所定部分に同様の凹状の文字3を形成した。次にイオンプレーティング法による青色系のTiO層10を1.5 μ m被覆した。次に実施例1と同方法によりCrN層をエッチング除去した。このときCrN層上のTiO層も同時にリフトアップされ、きれいに除去された。これにより最終的に図3に示すように白色金合金時計ケース表面の所定部分にTiOによる青色系を呈する凹状の文字と白色金合金素材による二色外観を有する時計ケースが形成された。該時計ケースは実施例1と同様の品質試験の結果、時計ケースとしての耐食性、耐摩耗性、耐擦傷性を十分満足できた。

【0019】(実施例4) 図4は本発明実施例の時計ケースの断面図である。ZrO₂セラミックよりなる時計ケース11の表面全体に、実施例2と同様にTi被膜を1.0 μ m被覆し、レーザー加工により時計ケースの所定部分に同様の凹状の模様7を形成した。次にイオンプレーティング法によるCrNC被膜12を1.5 μ m被覆した。次に実施例2と同方法によりTi層をエッチング除去した。このときTi層上のCrNC層も同時にリフトアップされ、きれいに除去された。これにより最終的に図4に示すように、セラミック時計ケース表面の所定部分にCrNCによるステンレス色を呈する凹状の模様とセラミック素材による二色外観を有する時計ケースが形成された。該時計ケースは実施例1と同様の品質試験の結果、時計ケースとしての耐食性、耐摩耗性、耐擦傷性を十分満足できた。

【0020】

【発明の効果】以上述べた如く、本発明によれば超硬、Pt、Pt合金、セラミック、白色金合金素材上にイオンプレーティング法により第一層としてTi系またはC

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r系被膜の内の一種を被覆した後に、選択的所定部分にレーザー加工により凹状の模様または文字を形成し、その後イオンプレーティング法により第二層として第一層被膜がTi系ではCr系被膜を被覆し、第一層被膜がCr系ではTi系の有色被膜を被覆し、引き続きエッチングによりTi系またはCr系の第一層被膜を剥離除去することにより、従来法の欠点であった外観品質の劣化およびコストアップを改善し、装飾部材の表面に複雑形状等の所望の有色を有する凹状の模様または文字を形成し他の部分を素材色に仕上げた二色外観を呈する、装飾的価値の高い装飾部材を品質的に安定で且つ安価に提供することが可能になった。適用に当たっては時計用文字板、針、バンド等の時計用外装部品はもちろんメガネフレーム、ライター、ネクタイピン、装身具等の装飾部品すべてに適用可能である。

【図面の簡単な説明】

【図1】 本発明による時計用外装部品の実施例の各製造工程を示す断面図。

【図2】 本発明による時計用外装部品の実施例の各製造工程を示す断面図。

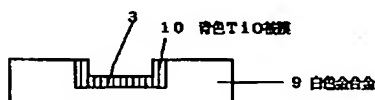
【図3】 本発明実施例による時計用外装部品の断面図。

【図4】 本発明実施例による時計用外装部品の断面図。

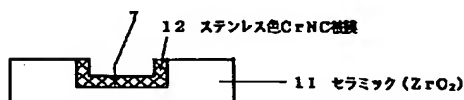
【符号の説明】

- 1 超硬(WC)
- 2 CrN被膜
- 3 レーザー加工文字
- 4 金色TiNC被膜
- 5 Pt合金(Pt-Cu)
- 6 Ti被膜
- 7 レーザー加工模様
- 8 灰黒色CrNCO被膜
- 9 白色金合金(Au-Ag-Pd)
- 10 青色系TiO被膜
- 11 セラミック(ZrO₂)
- 12 ステンレス色CrNC被膜

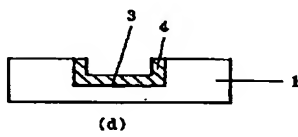
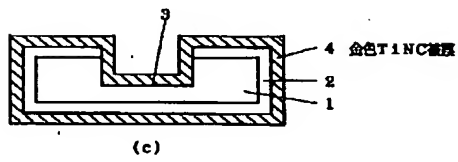
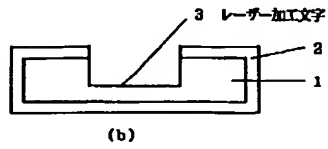
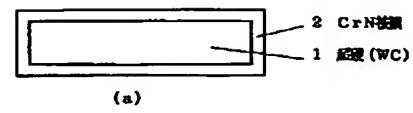
【図3】



【図4】



【図1】



【図2】

